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Oral Defense

High Surface Area Ti_4O_7 Supported Platinum Catalyst for Oxygen Reduction Reaction

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Outline

1. Introduction
2. Review of Previous Approach
3. Motivation and Approach
4. Result and Discussion
5. Conclusion
6. Outlook

Introduction

Energy Issue

Fossil fuels currently supply most of the world's energy needs

Energy flow diagram for the United States

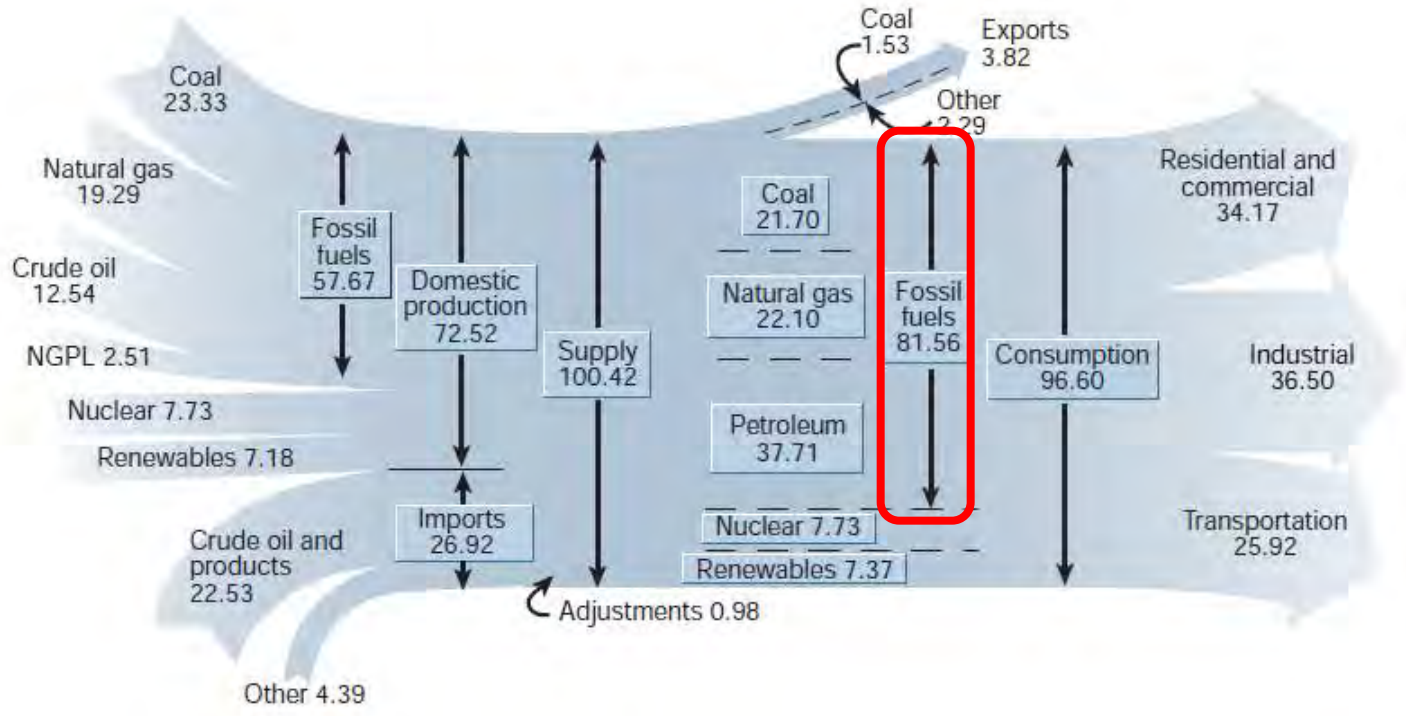


Fig. 1.1 P. 1

Hydrogen Energy

Challenges in realizing hydrogen fuel cell

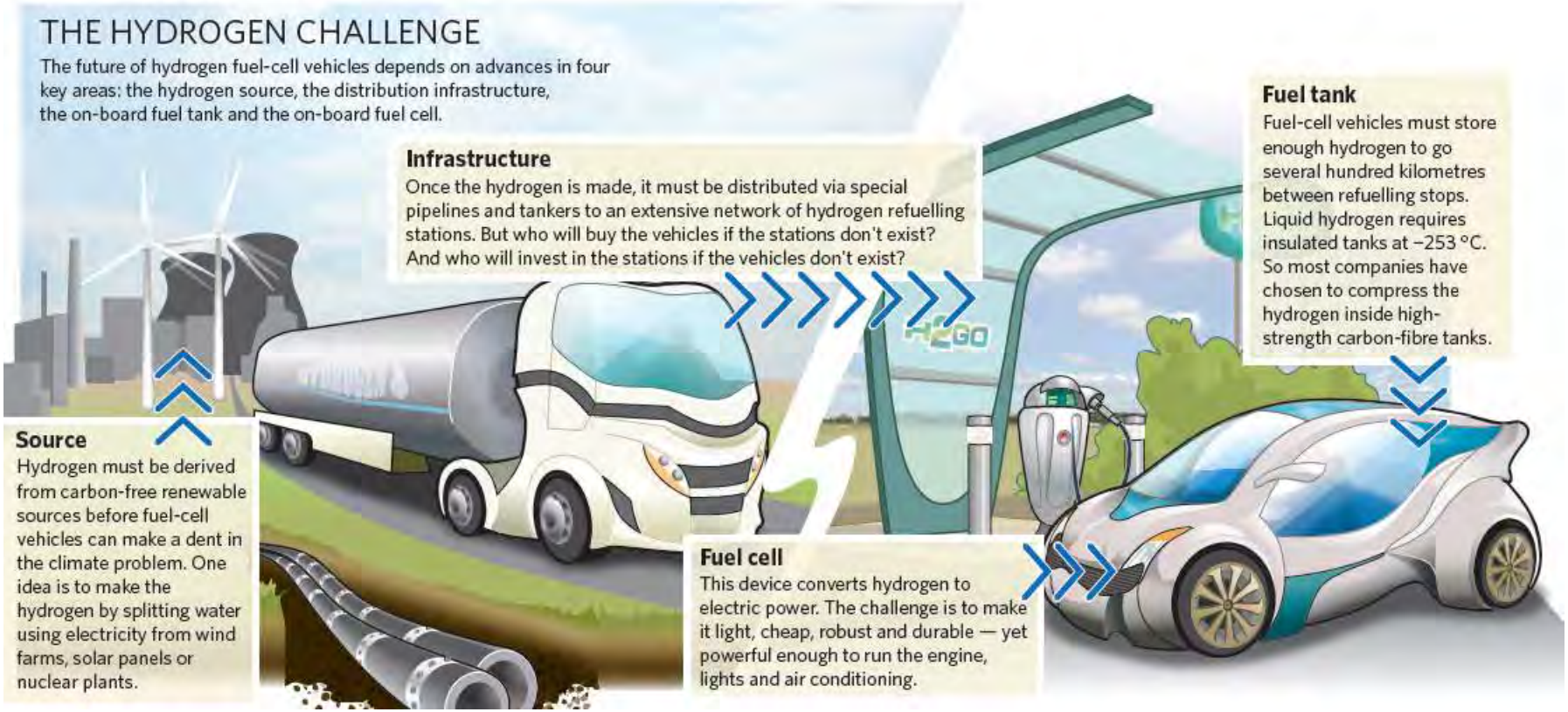
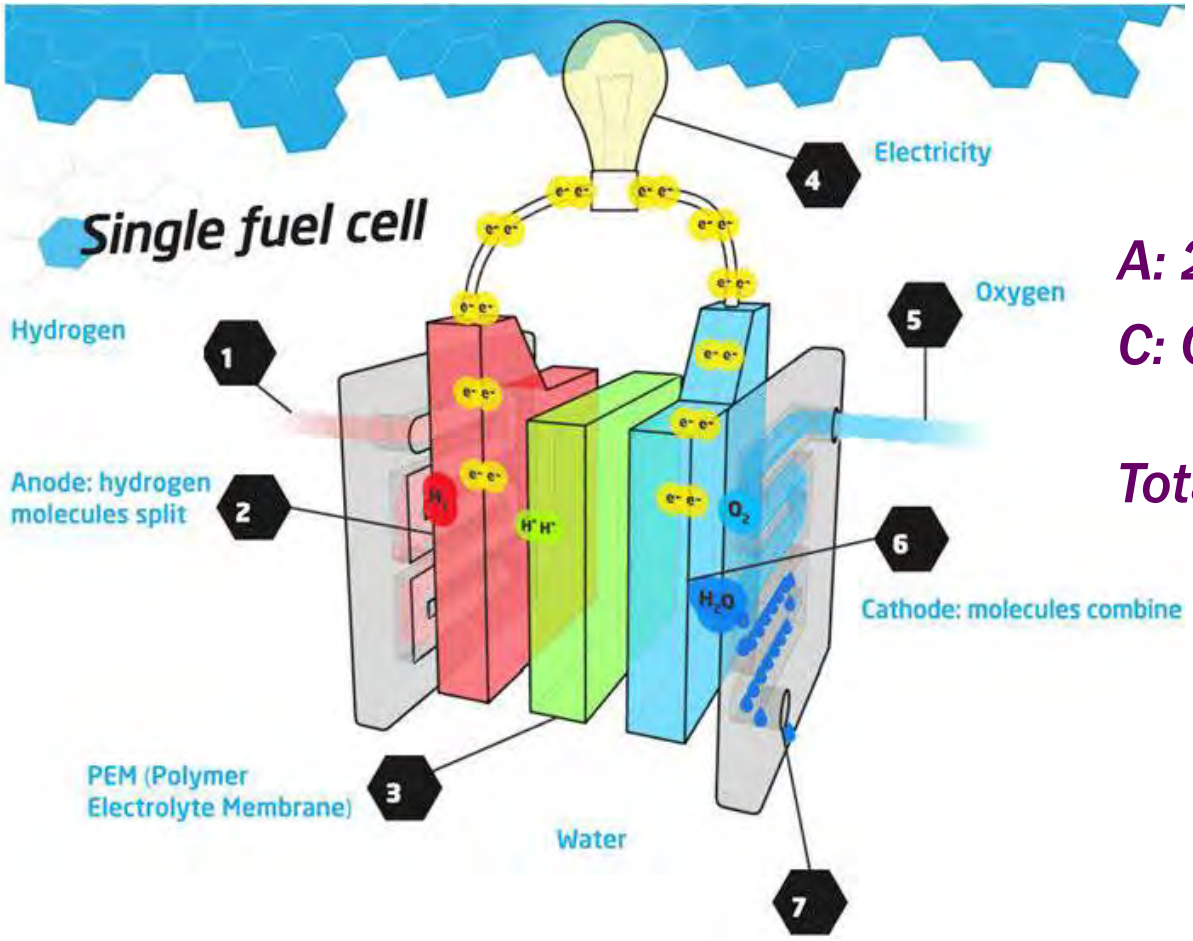


Fig. 1.2 P. 2

NATURE| VOL 464|29 APRIL 2010

Fuel Cell System



$A: 2H_2 \rightarrow 4H^+ + 4e^-$

$C: O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

$Total: 2H_2 + O_2 \rightarrow 2H_2O$

CO_2 free electricity

www.hyundailikesunday.com/2014/08/11/how-a-fuel-cell-vehicle-works/

Fuel Cell Catalyst Issues

In the catalyst point of view, there are two main issues toward wide commercialization of PEFCs.

The catalyst component:

1. *Active metal (Pt)*

Cost - Pt is expensive, solution:

- reducing Pt particle size
- alloying Pt with other metals
- utilizing non noble metals

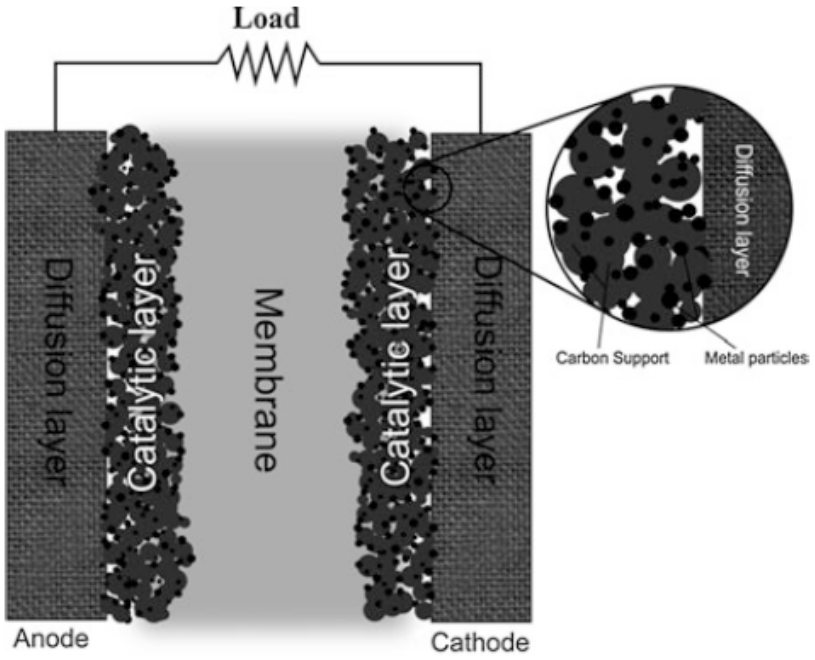


Fig. 2.2 P. 8

2. *Support material*

Performance - durability of electrocatalyst, solution:

- utilizing non carbon support

Carbon Corrosion

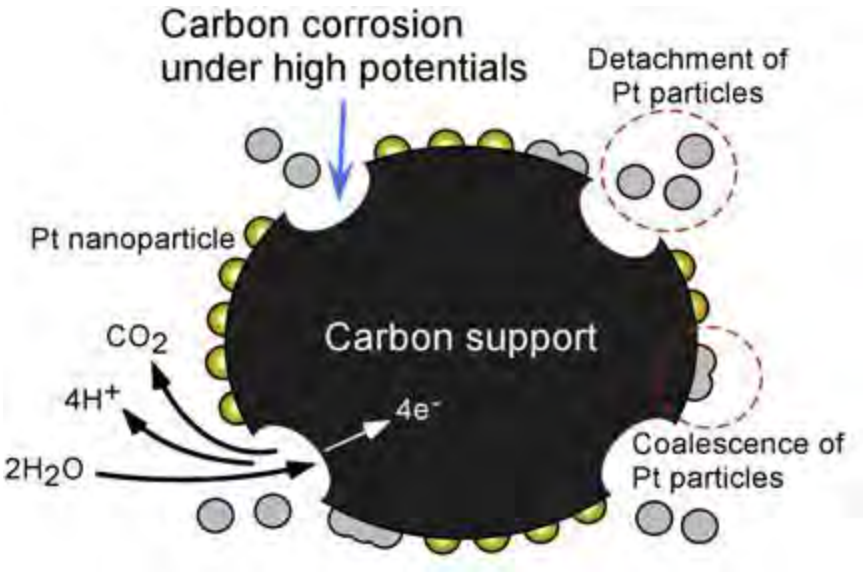


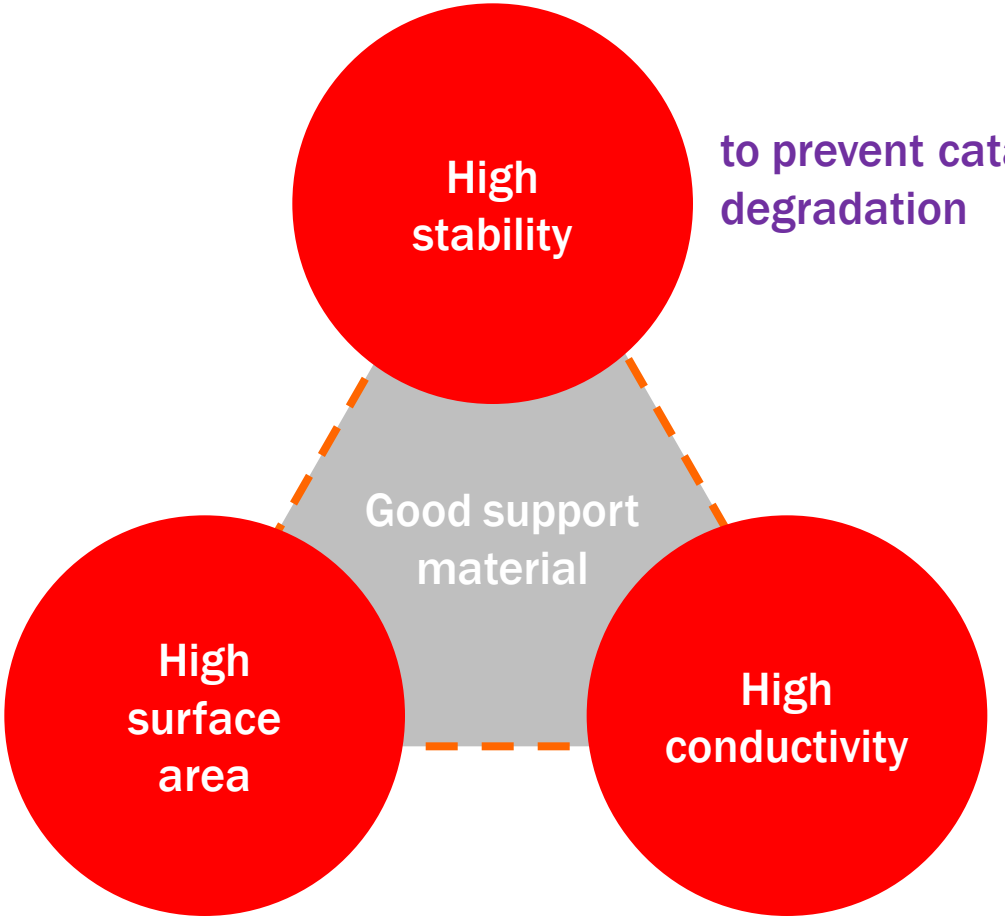
Fig. 1.4 P. 4

Carbon corrosion causes:

1. Catalyst coalescence
2. Detachment of catalyst particles from the carbon support material

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \quad E^0 = 0.207\ V\ vs.\ RHE\ at\ 25\ ^\circ C$$

Support Material Requirement



Ti_4O_7

Ti_4O_7 is substoichiometric titanium oxide. It has general formula Ti_nO_{2n-1} ($4<n<10$), which is known as Magnéli phase.

Ti_4O_7 is promising catalyst support material because:

1. High electronic conductivity
2. Stability

but, the surface area is low.

Review of Previous Approach

Challenges in Ti_4O_7 Synthesis

General route to synthesize Ti_4O_7:

Ti(IV) → reduced in high temperature → $Ti^{3.5+}$

High temperature synthesis

↓

Uncontrollable particle growth

↓

Low surface area

So, how to synthesize high surface area Ti_4O_7?

Recent Development of Ti_4O_7 Synthesis

1. *Reduction of TiO_2 in high temperature and H_2 atmosphere*

$$TiO_2 \xrightarrow[H_2\ gas]{1050\ ^\circ C\ (6\ h)} Ti_4O_7$$

Surface area: 0.95 $m^2\ g^{-1}$

Electrochemistry Communications 7 (2005) 183–188

$$TiO_2 \xrightarrow[H_2\ gas]{1050\ ^\circ C} Ti_4O_7$$

Surface area: 2 $m^2\ g^{-1}$

Journal of The Electrochemical Society, 155 (4) B321-B326 (2008)

$$TiO_2 \xrightarrow[H_2\ gas]{950\ ^\circ C\ (4\ h)} Ti_4O_7$$

Surface area: 2.7 $m^2\ g^{-1}$

Electrochimica Acta 55 (2010) 5891–5898

Advantage: carbon free, simple synthesis pathway

Disadvantage: low surface area

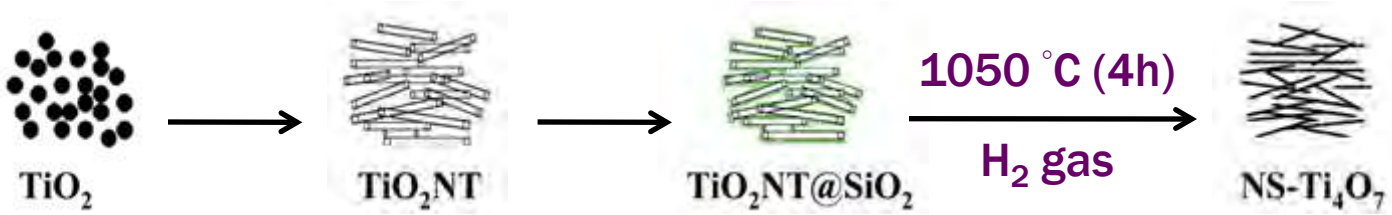
Recent Development of Ti_4O_7 Synthesis

2. *Modified reduction of TiO_2 in high temperature and H_2 atmosphere*

Ti(IV) isopropoxide —electrospinning→ TiO_2 nanofiber —1050 °C (6h), H_2 gas→ Ti_4O_7

Electrochimica Acta 59 (2012) 538–547

Surface area: 6 $m^2 g^{-1}$



J. Mater. Chem., 2012, 22, 16560–16565

Surface area: 26 $m^2 g^{-1}$

Advantage: higher surface area, carbon free

Disadvantage: multiple synthesis pathway

Recent Development of Ti_4O_7 Synthesis

3. *Reduction of Ti(IV) precursor in high temperature and inert atmosphere*

TiO_2 + carbon black $\xrightarrow[\text{vacuum}]{800\text{–}1{,}100\ ^\circ\text{C (2 h)}}$ Ti_4O_7

Surface area: ~4 $m^2\ g^{-1}$
Carbon content: n.a.

J Mater Sci: Mater Electron (2013) 24:4853–4856

Ti(IV) ethoxide + PEG 400 $\longrightarrow$ Ti composite $\xrightarrow[\text{Ar gas}]{950\ ^\circ\text{C}}$ Ti_4O_7

Surface area: 290 $m^2\ g^{-1}$
Carbon content: 15 wt%

Nature Communications (2014) 5:4759

Ti(IV) ethoxide + ethyleneimine $\longrightarrow$ Ti composite $\xrightarrow[\text{Ar gas}]{860\ ^\circ\text{C (3-4 h)}}$ Ti_4O_7

Surface area: 180 $m^2\ g^{-1}$
Carbon content: <2 wt%

Energy Environ. Sci., 2015,8, 1292-1298

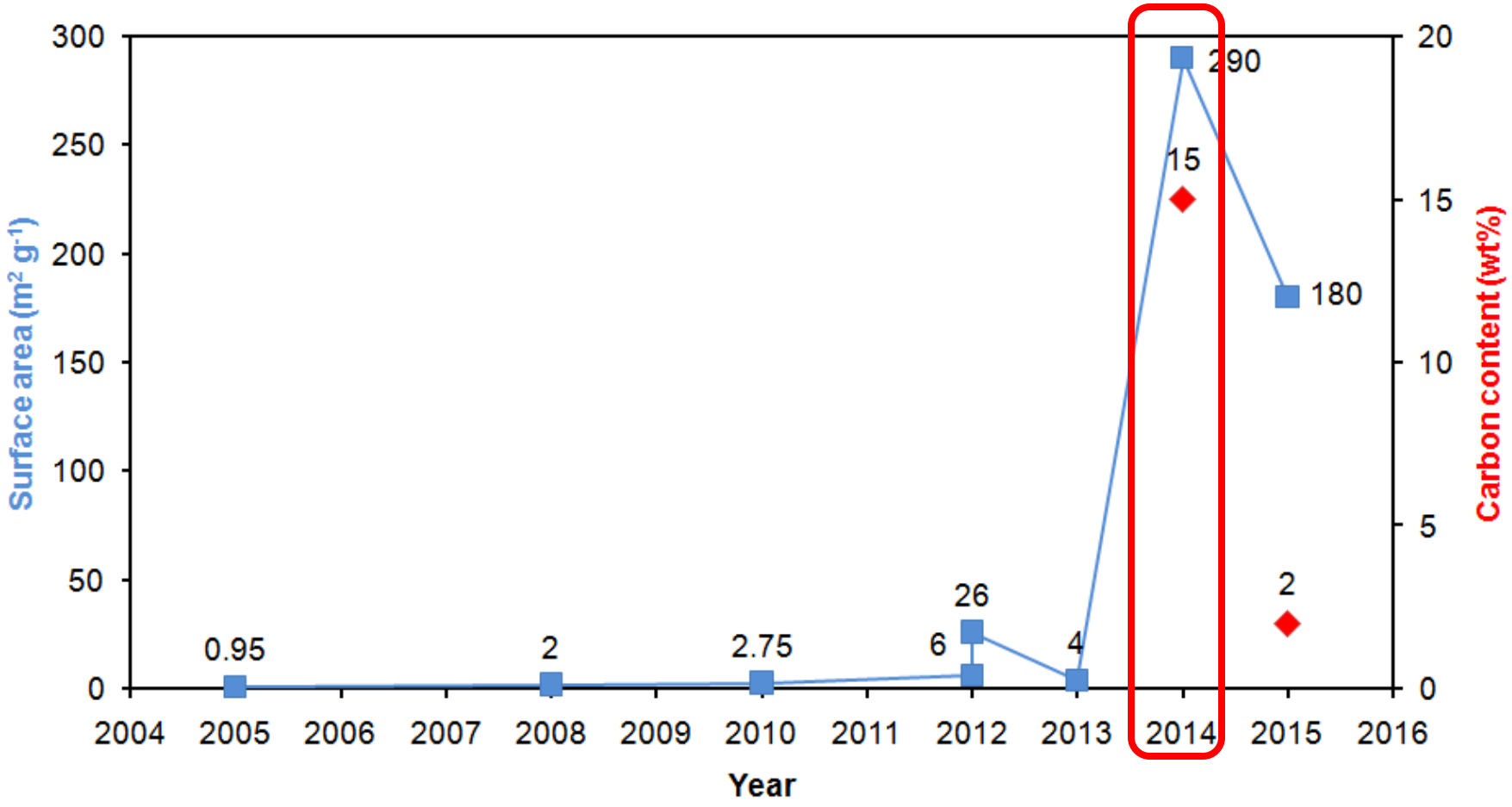
Advantage: high surface area, safer
Disadvantage: contains carbon

Summary of Ti_4O_7 Synthesis

Year	Ti(IV) precursor	Calcination condition			Reducing agent	Surface area ($m^2\ g^{-1}$)	Carbon content
		Temp (°C)	Time (hrs)	Gas			
2005	TiO_2	1050	6	H_2	H_2	0.95	0
2008	TiO_2	1050	n.a.	H_2	H_2	2	0
2010	TiO_2	950	4	H_2	H_2	2.75	0
2012	titanium(IV) isopropoxide	1050	6	H_2	H_2	6	n.a.
2012	TiO_2	1050	4	H_2	H_2	26	0
2013	TiO_2	800 - 1100	2	vacuum	carbon black	~4	n.a.
2014	titanium(IV) ethoxide	950	n.a.	Ar	PEG 400	290	15 wt%
2015	titanium(IV) ethoxide	860	3-4	Ar	ethylene-imine	180	<2 wt%

Table 2.2 P. 24

Roadmap of Ti_4O_7 Synthesis



Motivation and Approach

Motivation

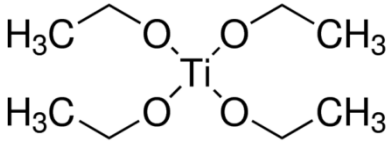
In this work, we want to synthesize high surface area Ti_4O_7 to support platinum catalyst for oxygen reduction reaction.

Therefore, the three requirement of good catalyst support can be achieved.

1. High surface area
2. Good electronic conductivity
3. Good stability

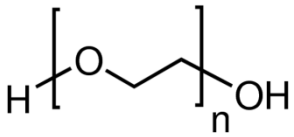
Approach

Ti_4O_7 Synthesis



Titanium(IV) ethoxide

+



Poly(ethylene glycol) 400

EtOH

stir at 60-80 ˚C
for 12 hours

followed by

drying at 100 ˚C
for 6 hours

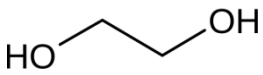
white powder

Ar

calcination at 950 ˚C
for 4 hours

Ti_4O_7

Pt Deposition



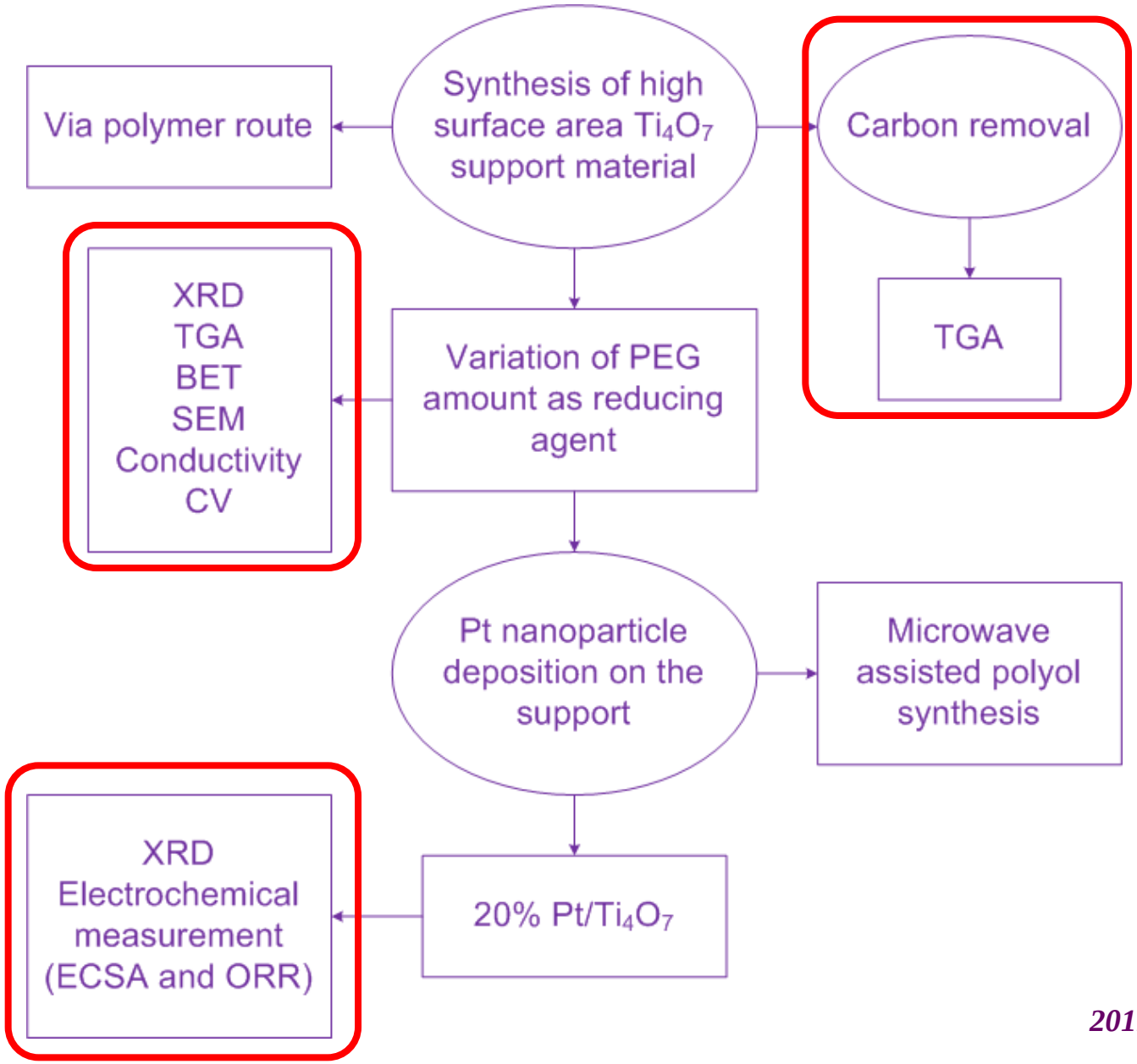
ethylene glycol

$H_2PtCl_6 \cdot 6H_2O$ + Ti_4O_7

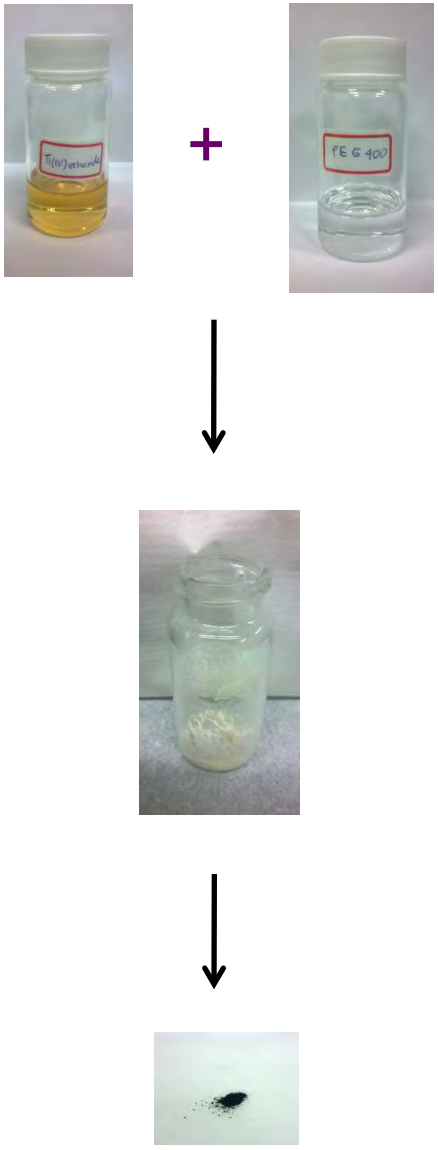
stir at 160 ˚C
for 1 hours
in microwave

20% Pt/Ti_4O_7

Experimental Framework



Flowchart of Ti_4O_7 Synthesis



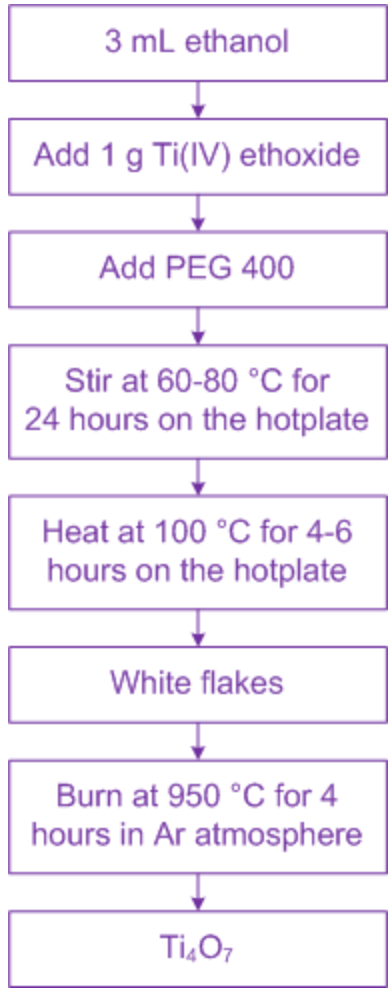


Fig. 3.1 P. 27

Flowchart of Platinum Deposition

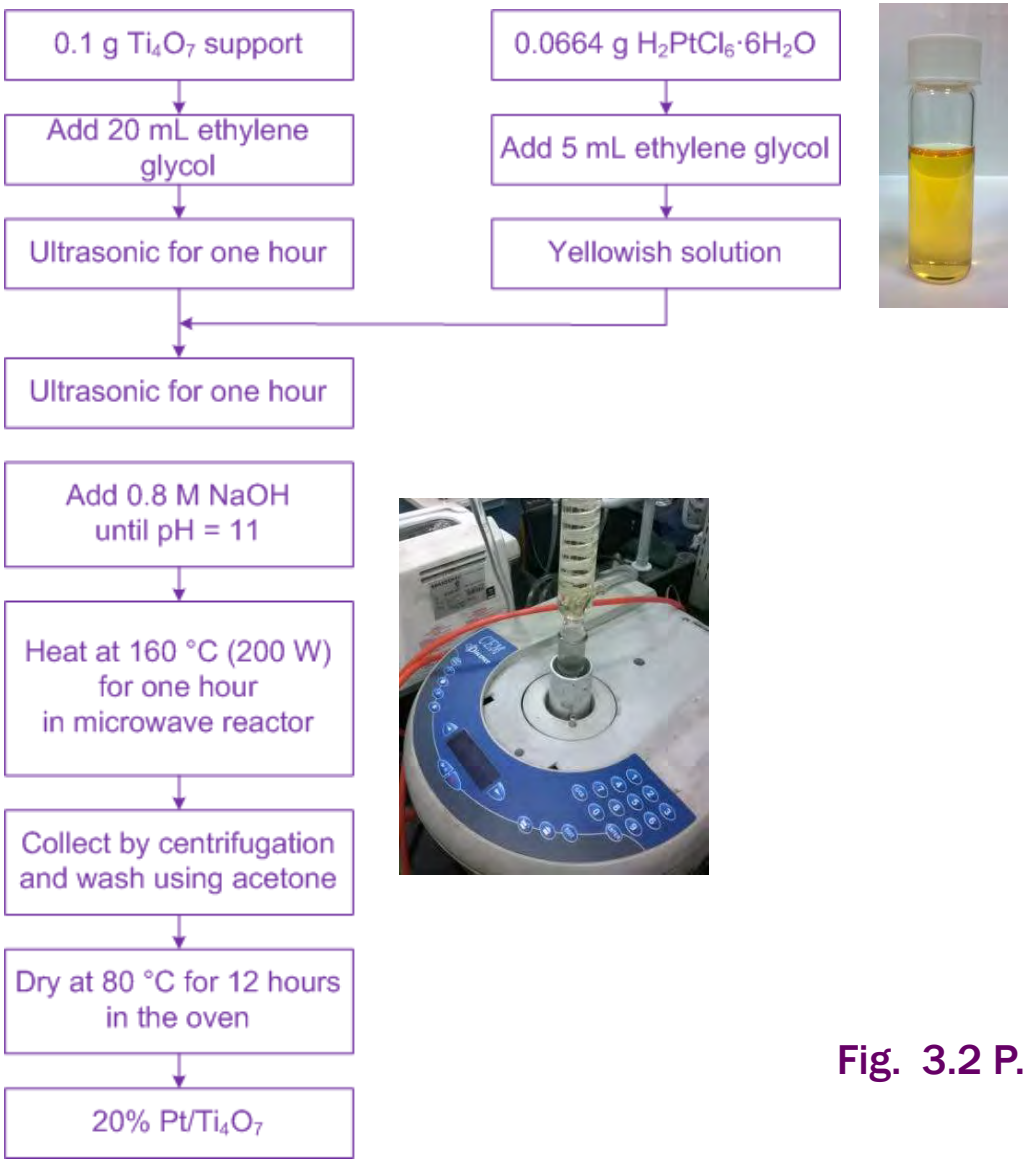


Fig. 3.2 P. 28

Flowchart of Carbon Removal

Extraction treatment

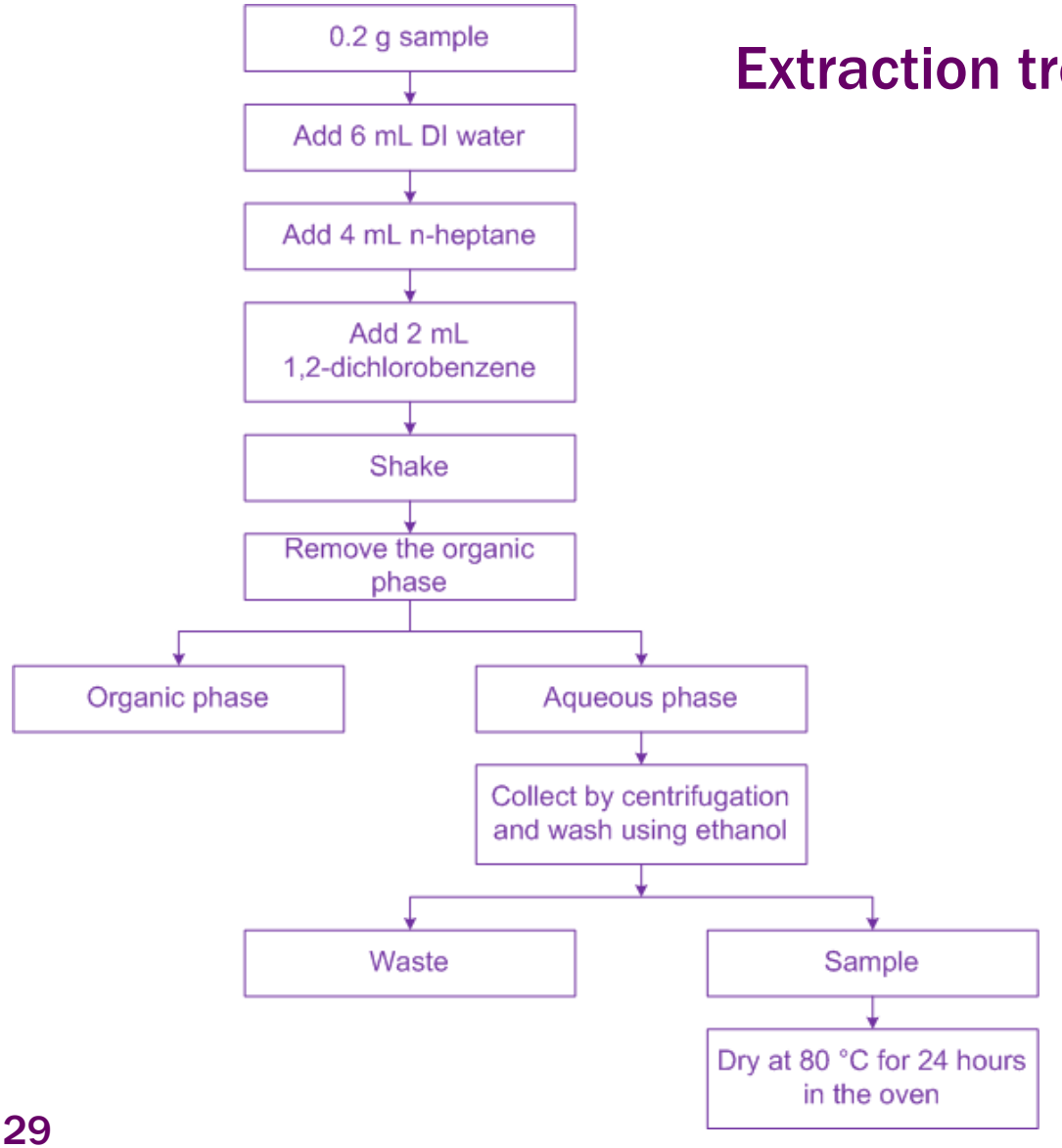


Fig. 3.3 P. 29

Flowchart of Carbon Removal

Solvent treatment

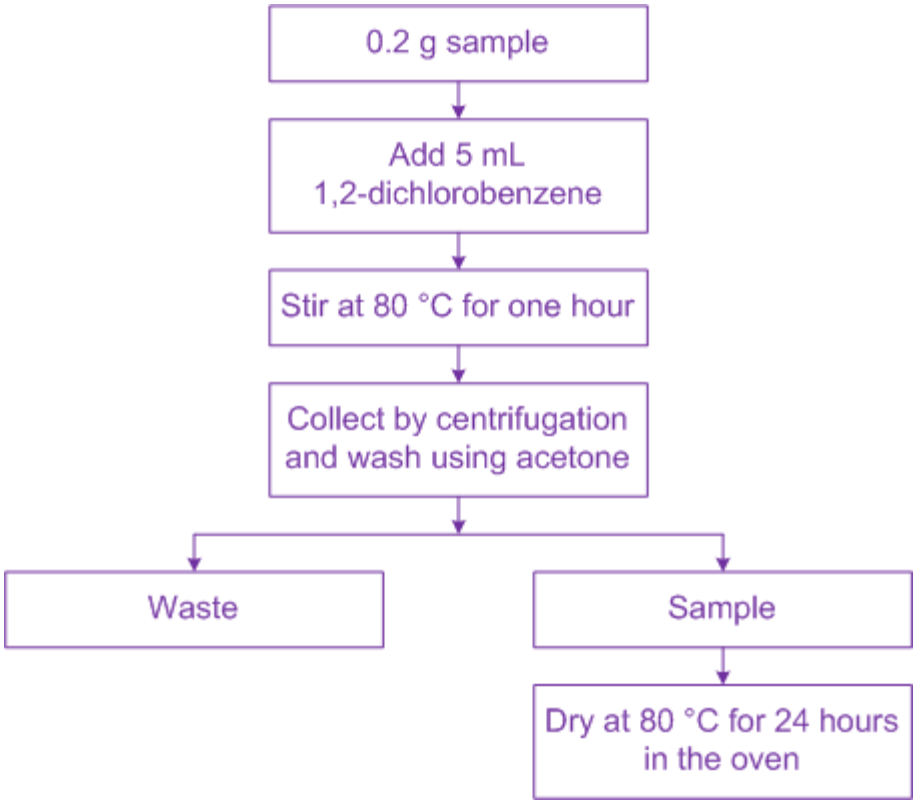


Fig. 3.4 P. 30

Flowchart of Carbon Removal

Acid treatment

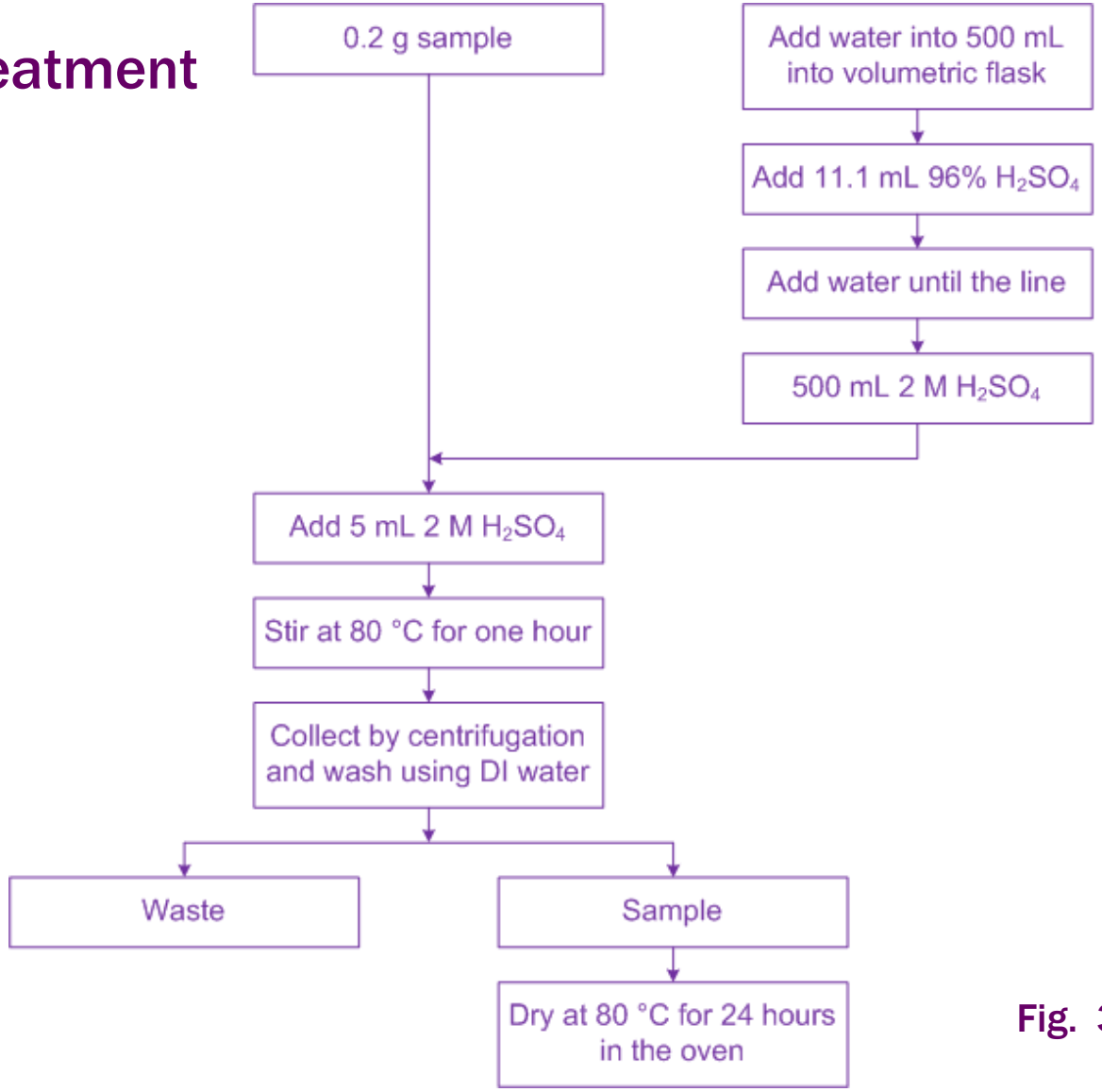


Fig. 3.5 P. 31

Flowchart of Carbon Removal

Base treatment

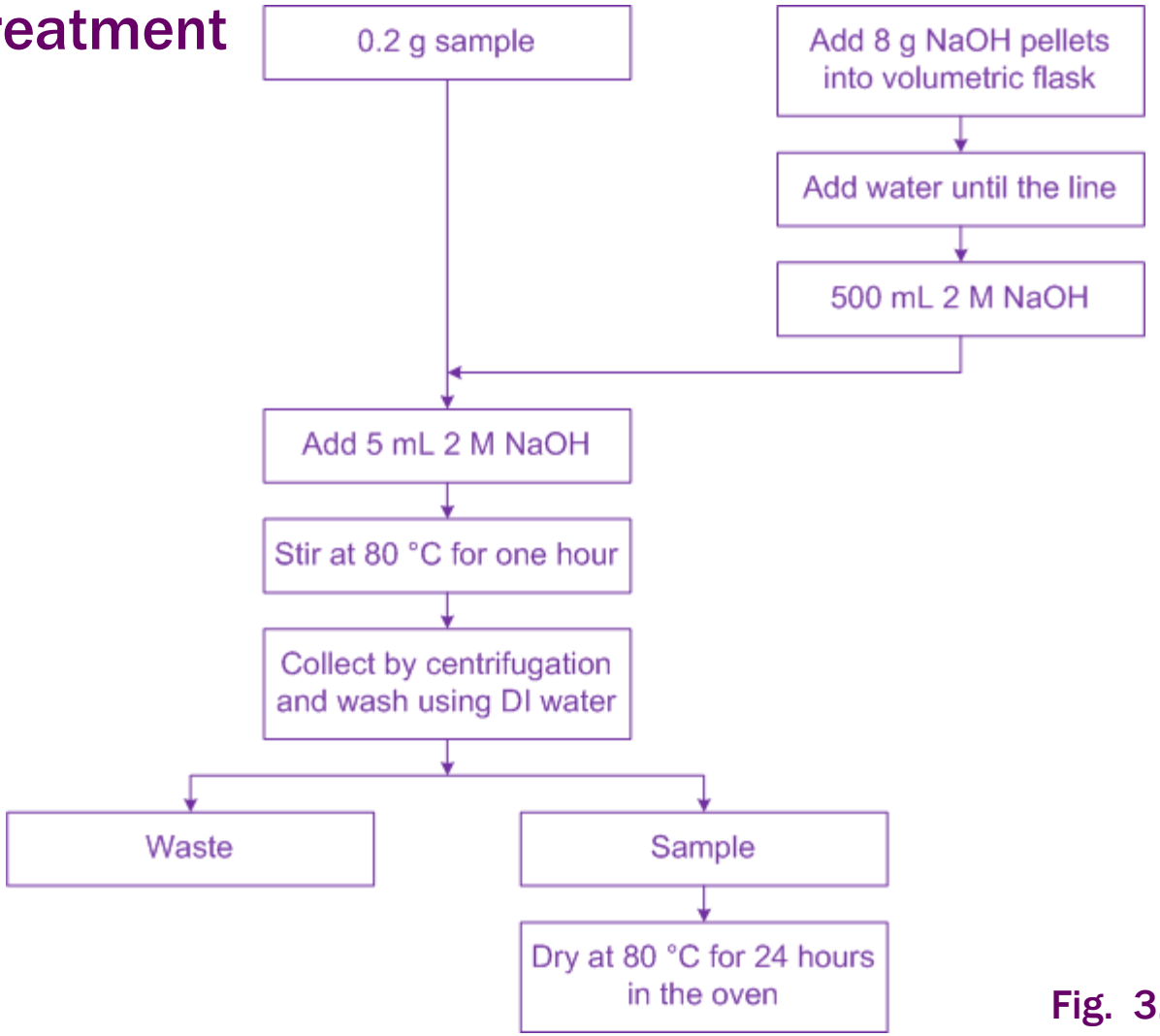
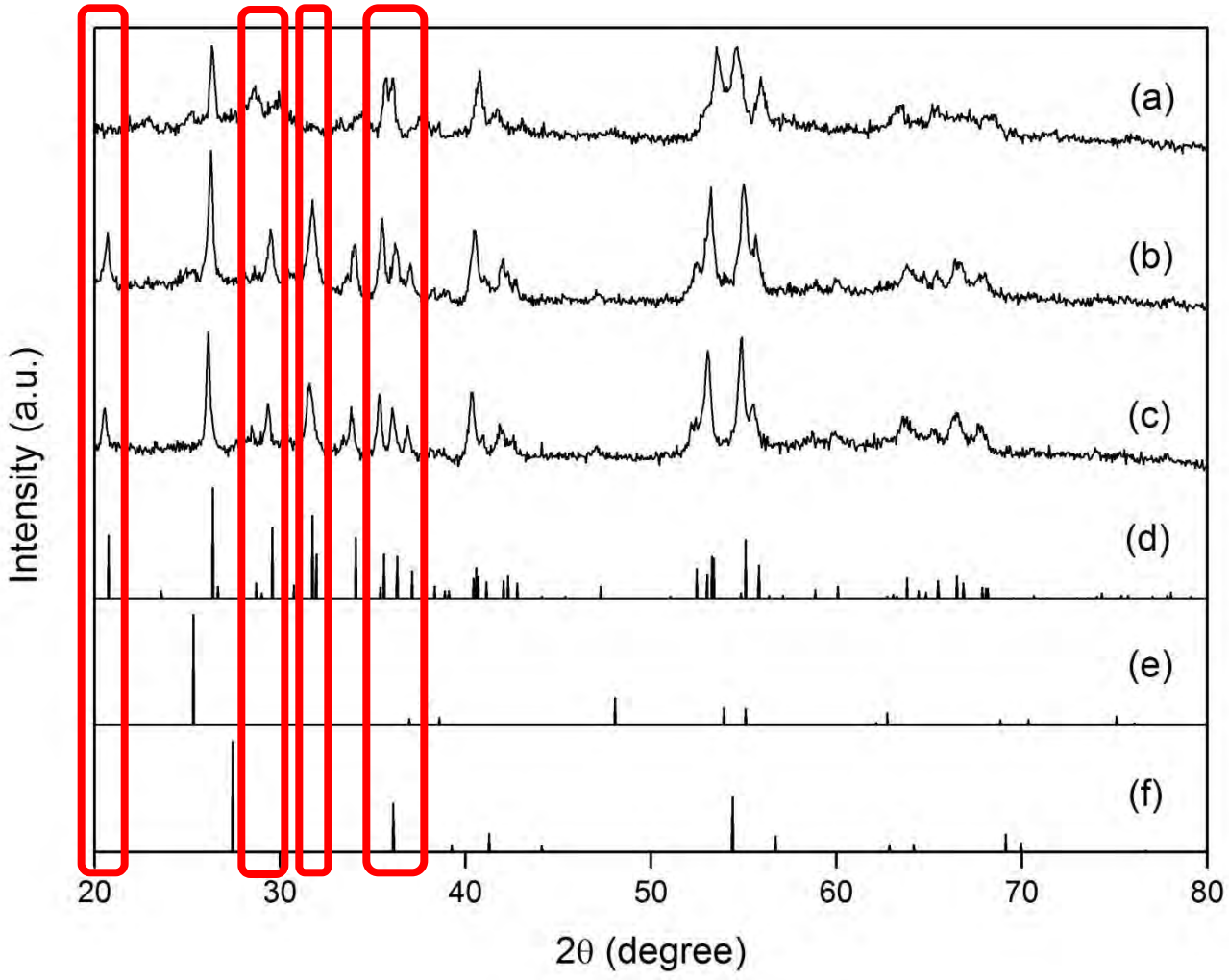


Fig. 3.6 P. 31

Result and Discussion

Ti_4O_7 Support Material

XRD



Ti10PEG03

Ti10PEG04

Ti10PEG05

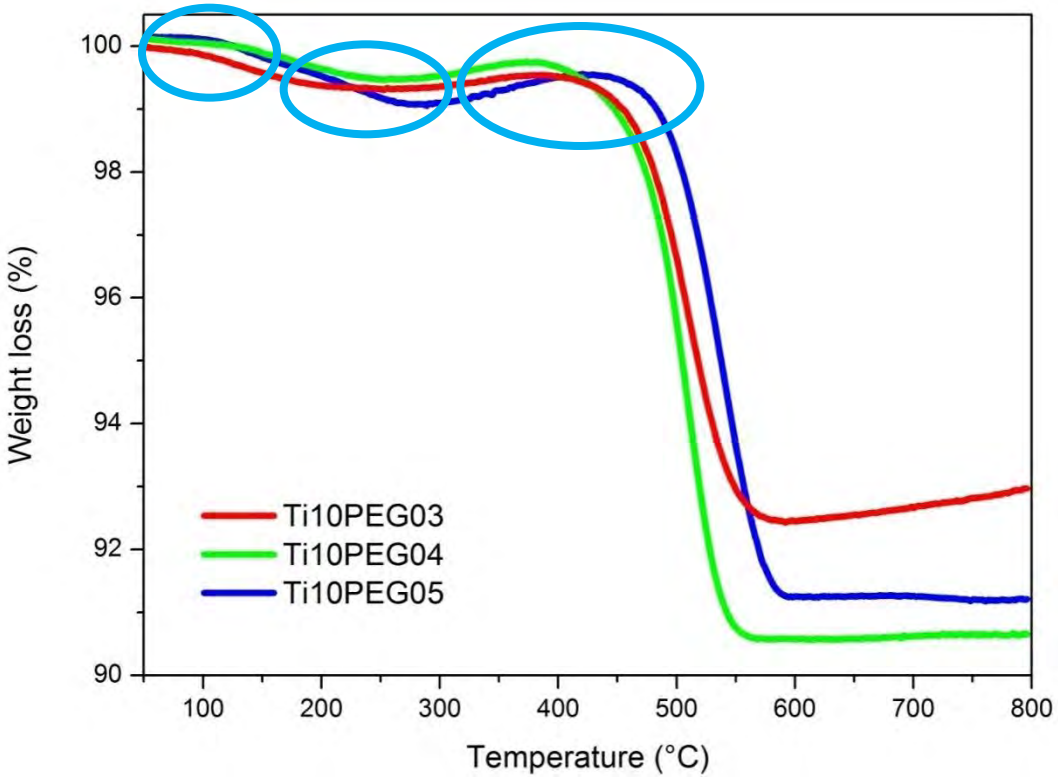
Ti_4O_7 (PDF 50-0787)

anatase-TiO2 (PDF 84-1286)

rutile-TiO2 (PDF 84-1284)

Fig. 4.1 P. 38

TGA and Conductivity



The increasing weight is caused by oxidation of Ti_4O_7 to the more stable TiO_2 phase.

Fig. 4.2 P. 40

Sample	Decomposition (%)
Ti10PEG03	7.57
Ti10PEG04	9.44
Ti10PEG05	8.82

Table 4.1 P. 41

Sample	Conductivity (S cm^{-1})
Ti10PEG03	95.47
Ti10PEG04	172.96
Ti10PEG05	113.43

Table 4.3 P. 45

Physisorption Analysis

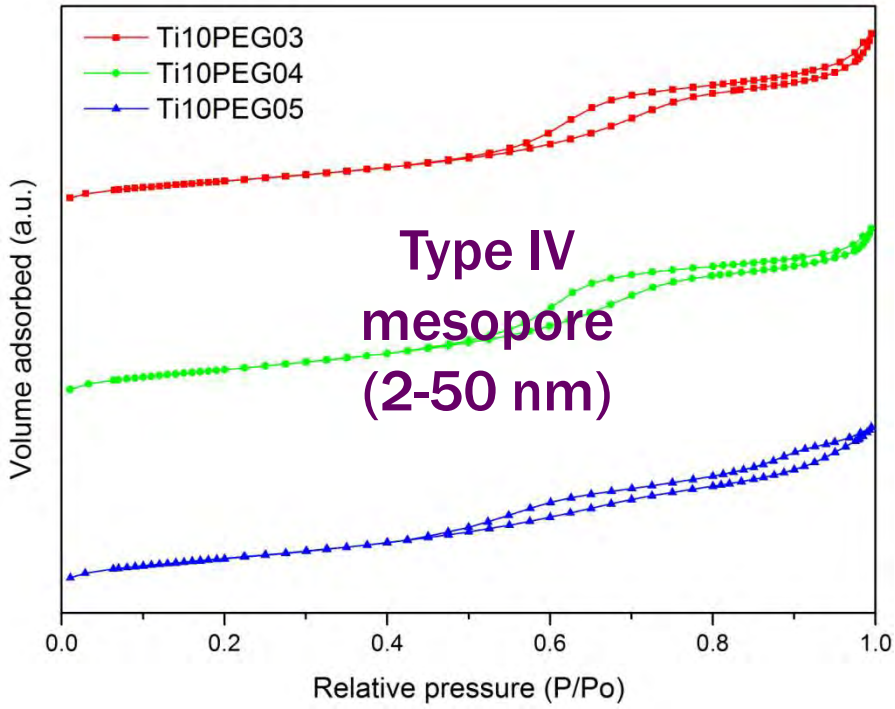


Fig. 4.3 P. 42

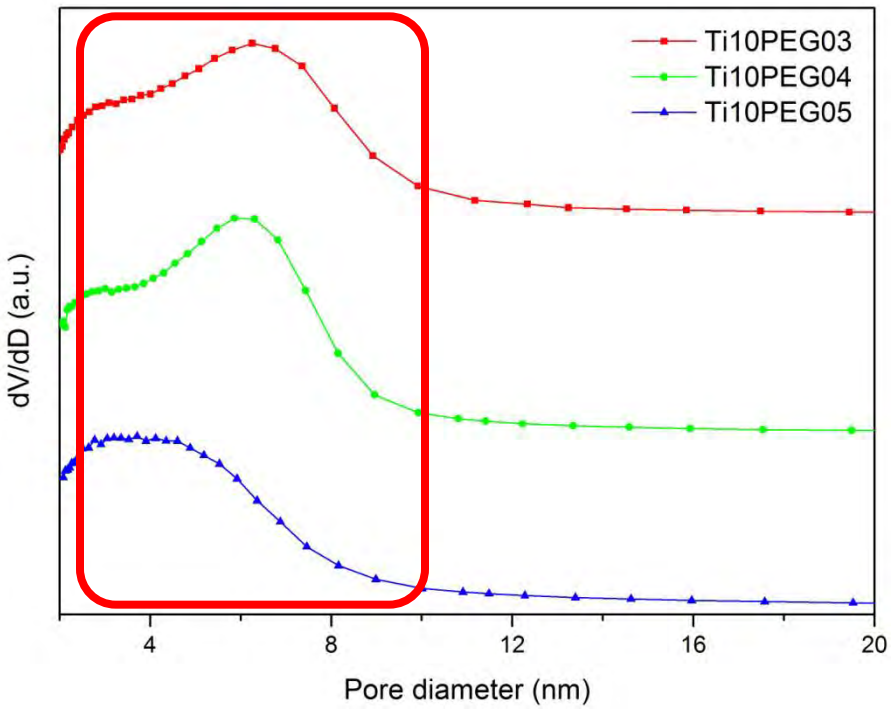


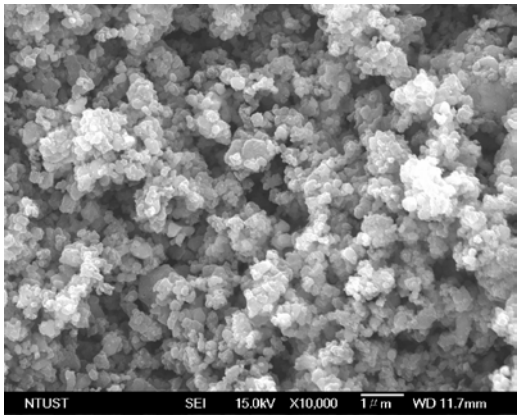
Fig. 4.4 P. 43

Sample	BET surface area (m^2 g^{-1})
Ti10PEG03	154.9
Ti10PEG04	187.6
Ti10PEG05	178.3

Table 4.2 P. 44

SEM Images

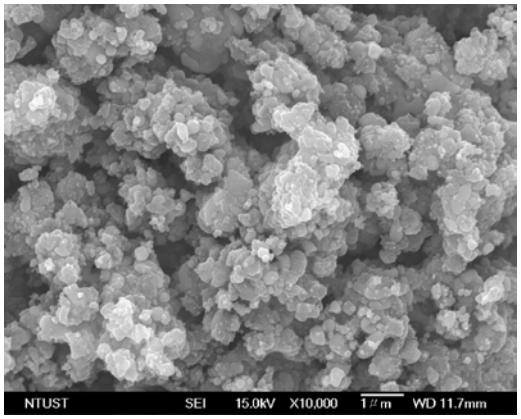
Ti10PEG03



The sample morphology seems to be built from many granules.

It indicates the PEG was successfully inhibit the formation of large particle during heat treatment.

Ti10PEG04



Ti10PEG05

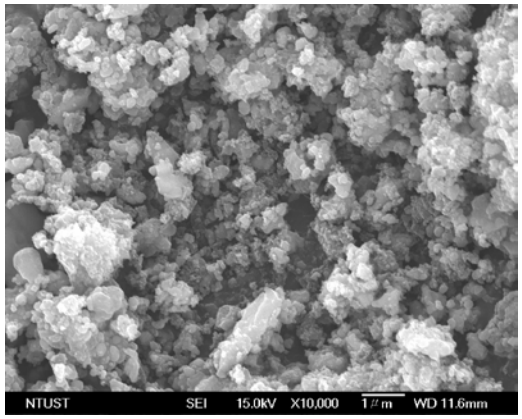
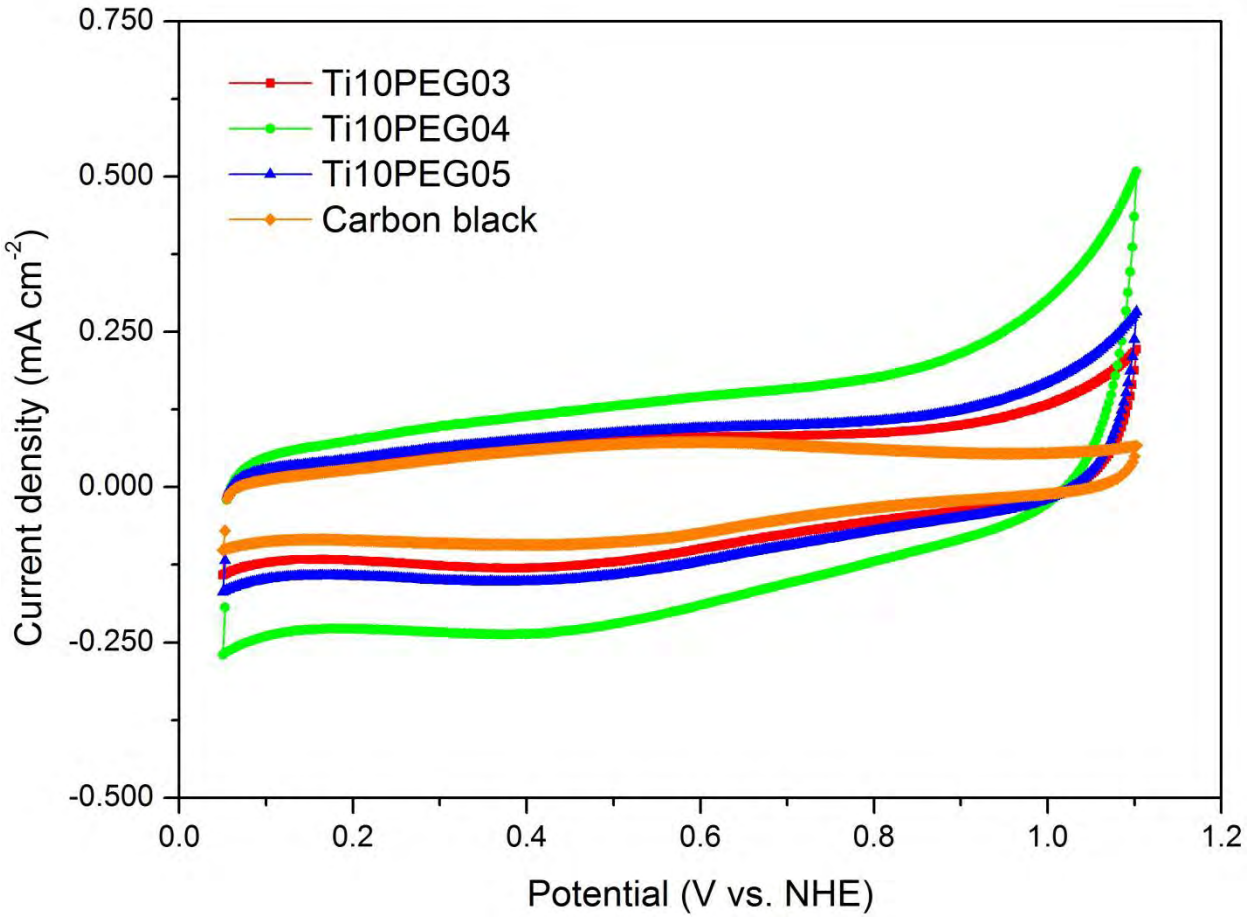


Fig. 4.5 P. 44

Cyclic Voltammetry



No oxidation peaks are observed indicates the stability of Ti_4O_7 support materials.

Fig. 4.6 P. 46

Summary

1. *Based on XRD results, the best Ti(IV) ethoxide and PEG 400 ratio in Ti_4O_7 synthesis was 10:4 weight ratio.*
2. *SEM images clearly show that the entire samples had pore structure.*
3. *CV analysis results revealed that the entire samples were stable in acidic environment.*

Sample	Carbon residue (%)	BET surface area ($m^2\ g^{-1}$)	Conductivity ($S\ cm^{-1}$)
Ti10PEG03	7.57	154.9	95.47
Ti10PEG04	9.44	187.6	172.96
Ti10PEG05	8.82	178.3	113.43

Result and Discussion

Carbon Removal

Carbon Removal by Extraction Treatment

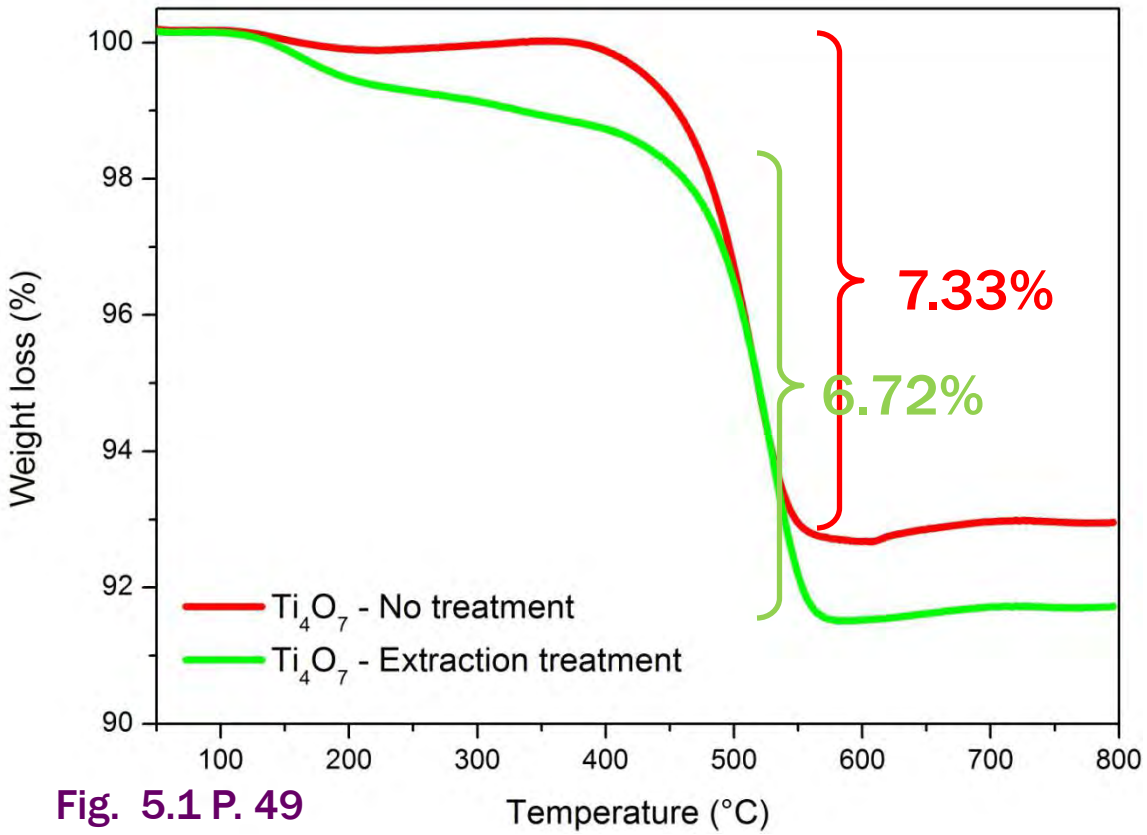
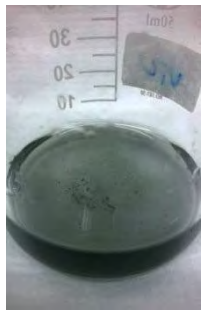


Fig. 5.1 P. 49

mixture of n-heptane ($d = 0.68\ g\ mL^{-1}$) and 1,2-dichlorobenzene ($d = 1.30\ g\ mL^{-1}$)

after extraction



removed organic phase

Carbon Removal by Solvent Treatment

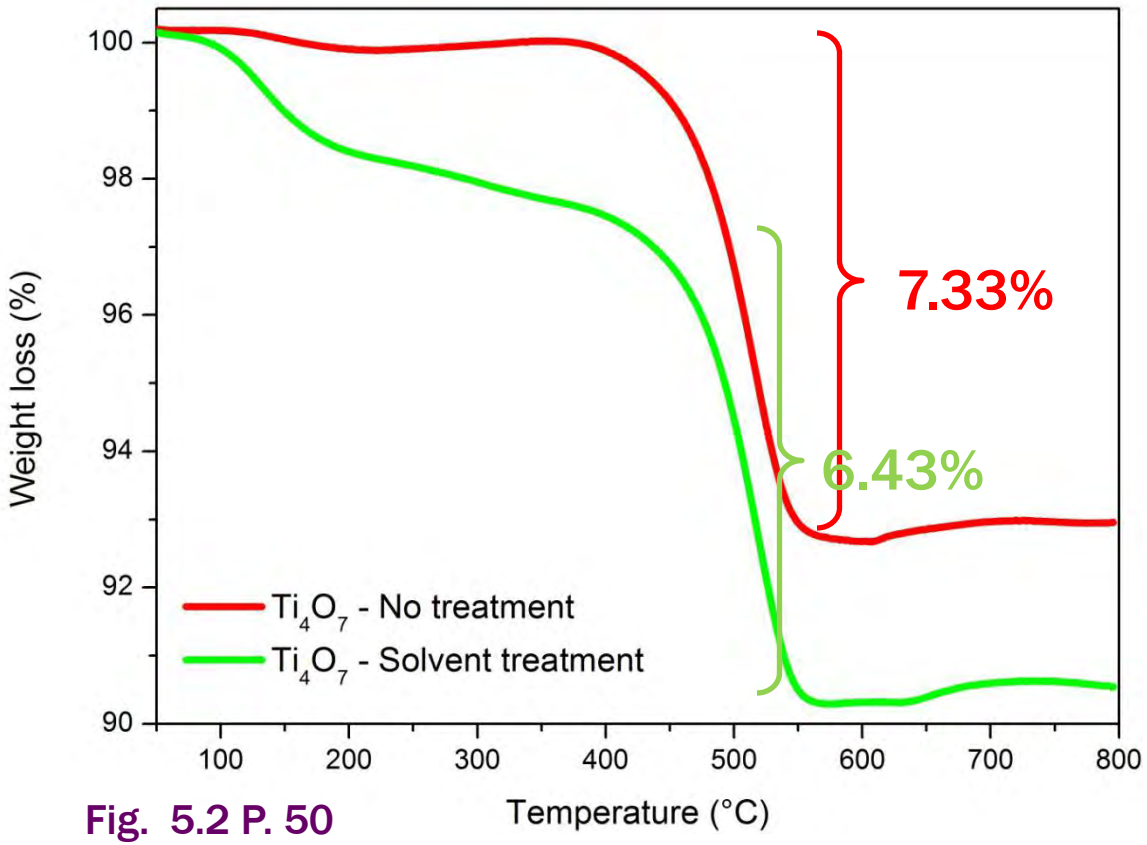


Fig. 5.2 P. 50

The decreasing decomposition after treatment indicates some carbon have been dissolved in the solvent and removed from Ti_4O_7 support material.

collected solvent after centrifugation

mixture of Ti_4O_7 and 1,2-dichlorobenzene

Carbon Removal by Acid-base Treatment

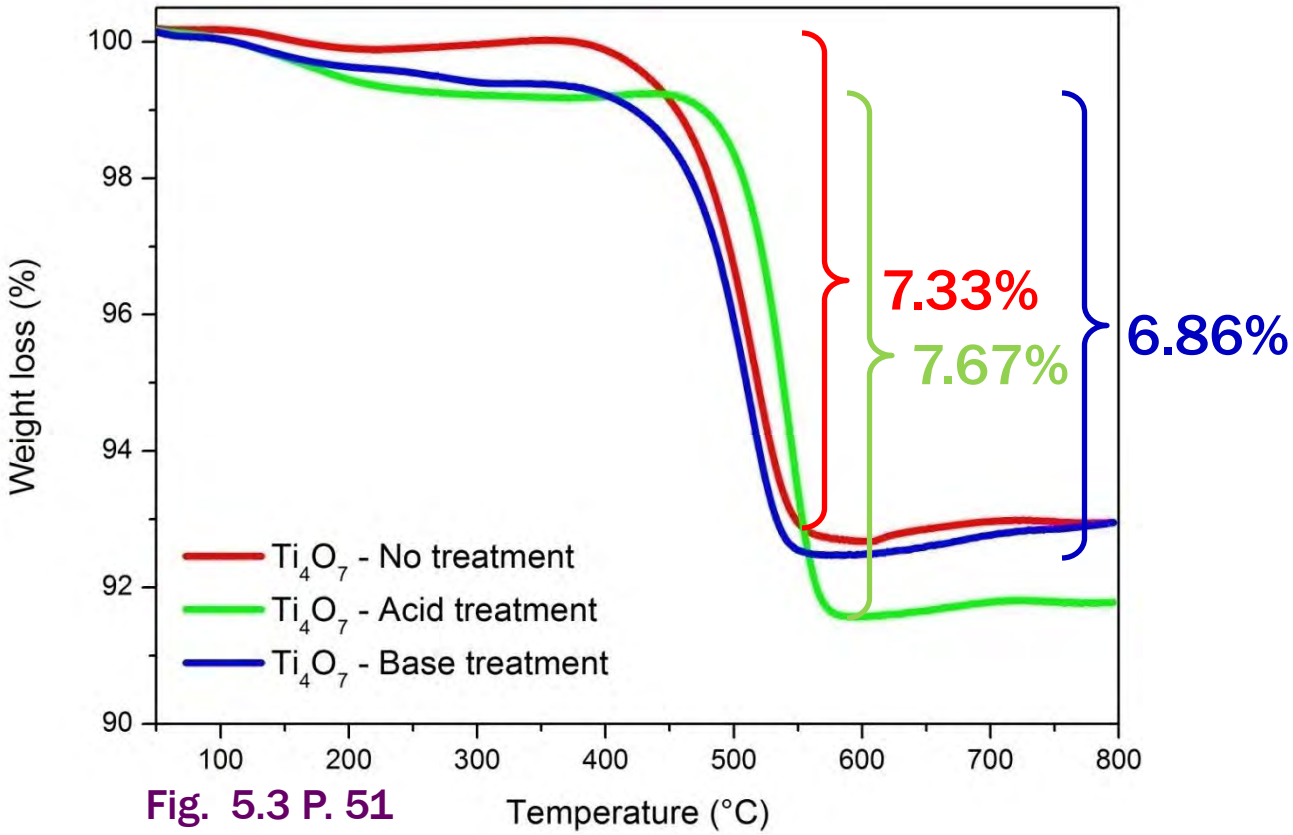
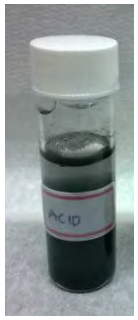


Fig. 5.3 P. 51

The increasing weight after acid treatment indicates sulfuric acid area trapped in the Ti_4O_7 support material.

collected acid-base after centrifugation



mixture of Ti_4O_7 and 2M H_2SO_4

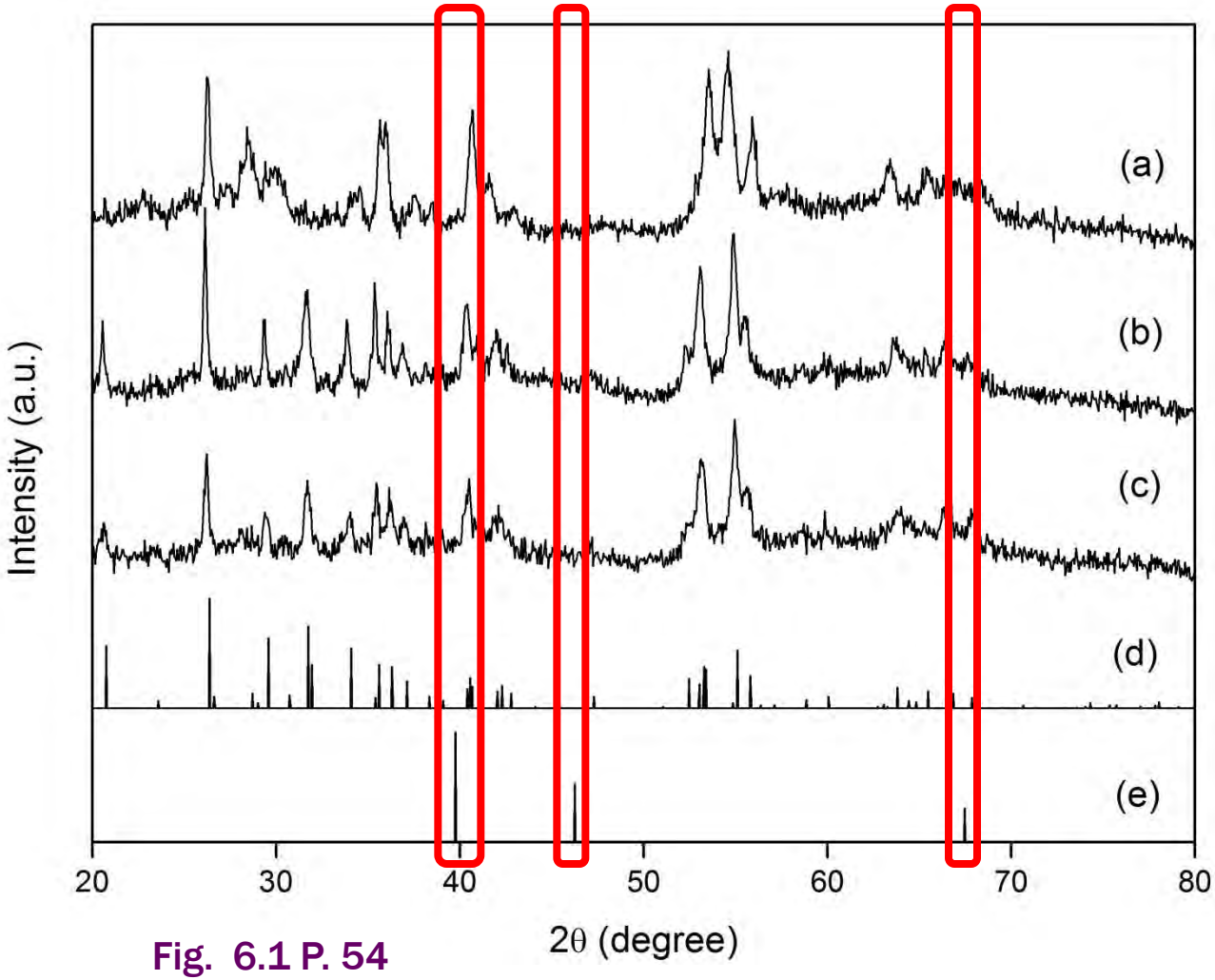
Summary

1. *Based on the thermogravimetric analysis results, the carbon was not completely removed from Ti_4O_7 support material.*
2. *Increasing decomposition after acid treatment indicated that the sulfuric acid was trapped in the Ti_4O_7 support material.*
3. *The best carbon removal was achieved by solvent treatment which successfully removed 12.28% carbon from Ti_4O_7 support material.*

Result and Discussion

20% Pt/Ti_4O_7 Catalyst

20% Pt/Ti_4O_7 Characterization



20% Pt/Ti10PEG03

20% Pt/Ti10PEG04

20% Pt/Ti10PEG05

Ti_4O_7 (PDF 50-0787)

Platinum (PDF 04-0802)

Fig. 6.1 P. 54

Electrochemical Measurement Result

0.5% Nafion 117

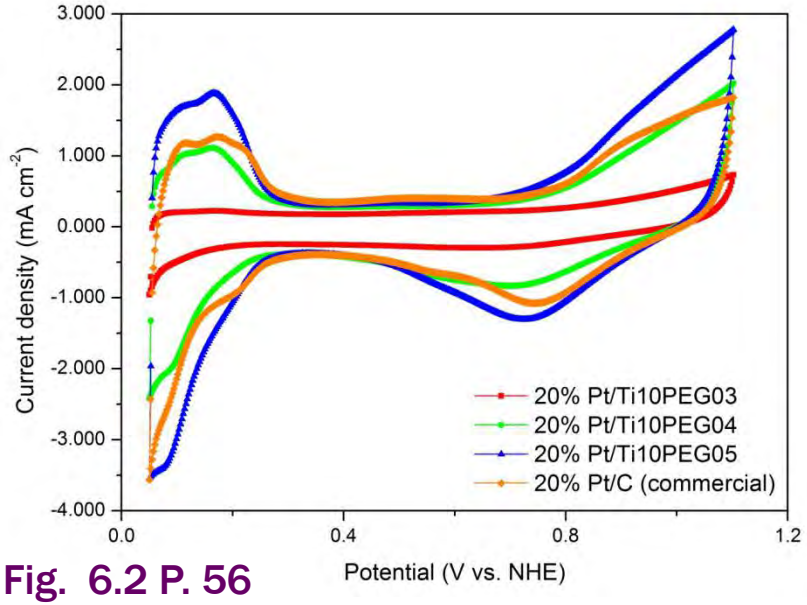


Fig. 6.2 P. 56

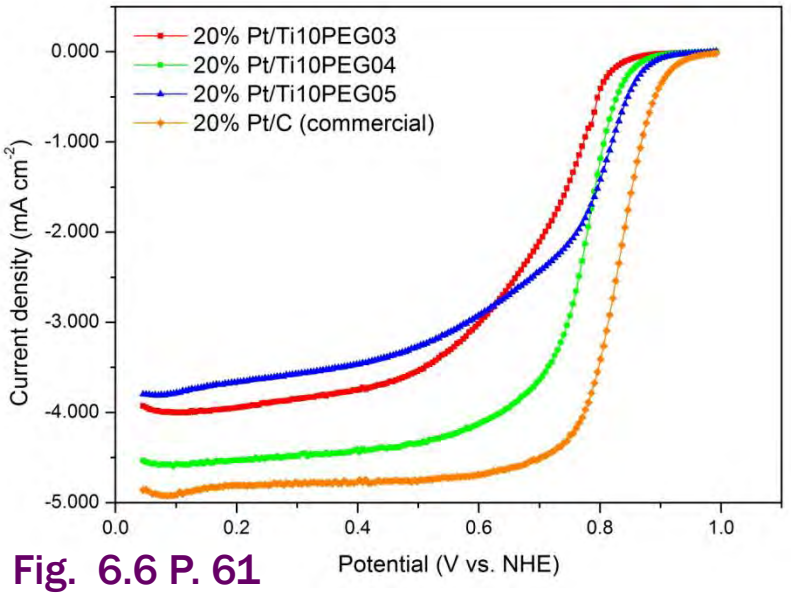


Fig. 6.6 P. 61

Sample	ECSA ($m^2\ g^{-1}$)	Onset Potential (V)	Current density at 0.9 V ($mA\ cm^{-2}$)
20% Pt/Ti10PEG03	2.72	0.82	0.01884
20% Pt/Ti10PEG04	10.38	0.84	0.03534
20% Pt/Ti10PEG05	15.55	0.87	0.06851
20% Pt/C	11.99	0.89	0.34395

Electrochemical Measurement Result

0.1% Nafion 117

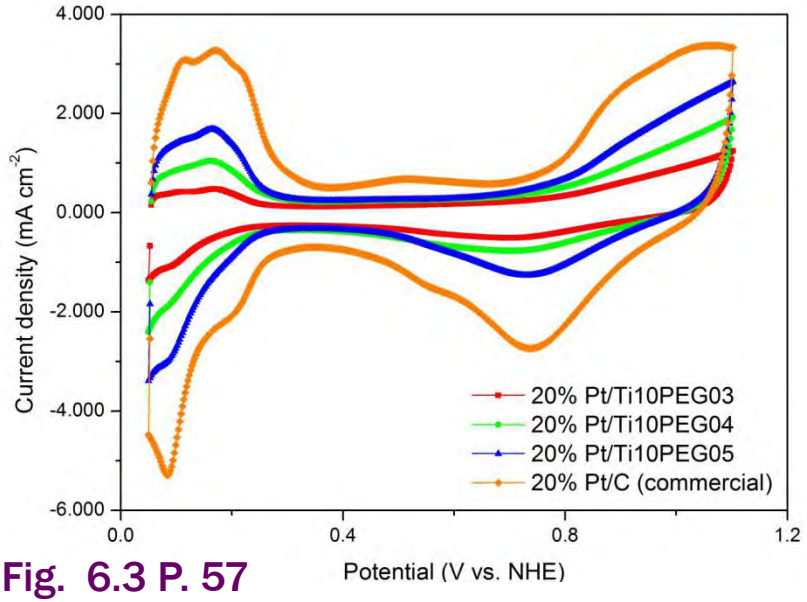


Fig. 6.3 P. 57

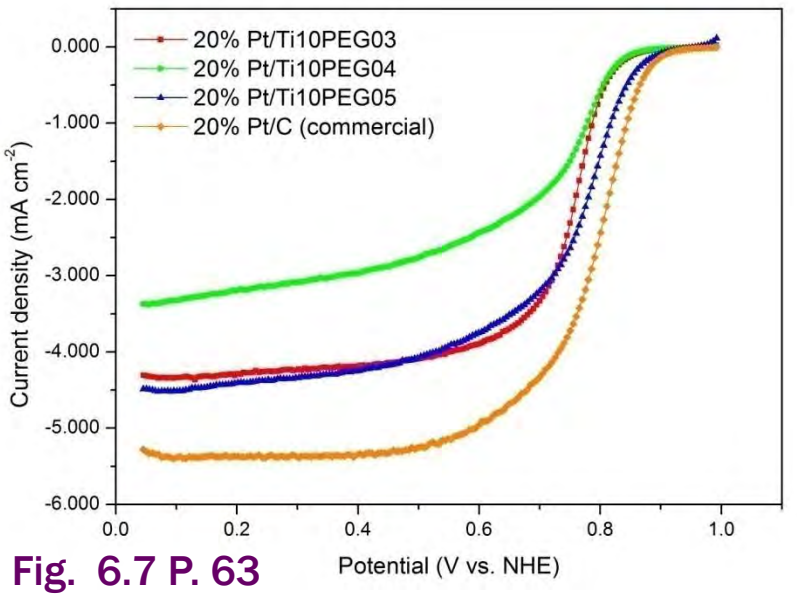


Fig. 6.7 P. 63

Sample	ECSA ($m^2\ g^{-1}$)	Onset Potential (V)	Current density at 0.9 V ($mA\ cm^{-2}$)
20% Pt/Ti10PEG03	3.65	0.83	0.02569
20% Pt/Ti10PEG04	8.44	0.82	0.01962
20% Pt/Ti10PEG05	13.45	0.86	0.07988
20% Pt/C	30.55	0.89	0.12643

Electrochemical Measurement Result

IPA:DI water (95:5)

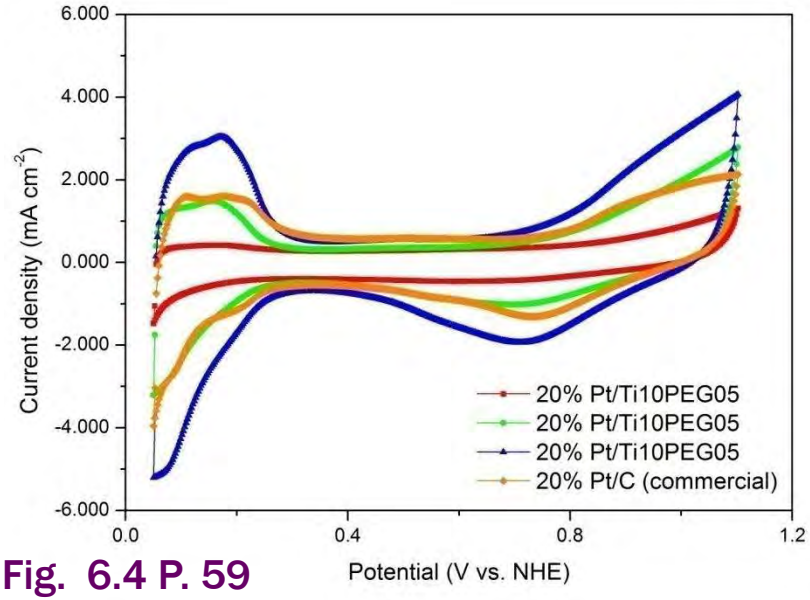


Fig. 6.4 P. 59

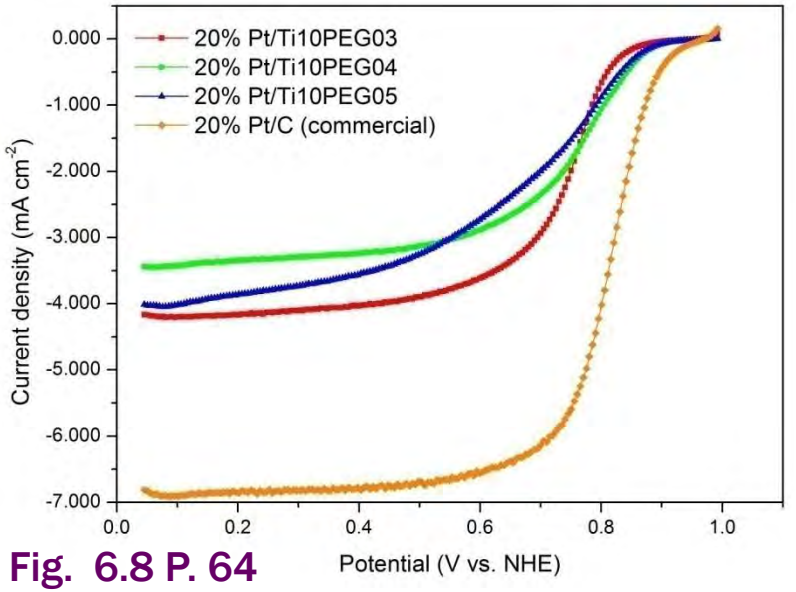


Fig. 6.8 P. 64

Sample	ECSA ($m^2\ g^{-1}$)	Onset Potential (V)	Current density at 0.9 V ($mA\ cm^{-2}$)
20% Pt/Ti10PEG03	4.69	0.82	0.03285
20% Pt/Ti10PEG04	12.61	0.87	0.07552
20% Pt/Ti10PEG05	26.22	0.88	0.06695
20% Pt/C	17.35	0.89	0.41588

Summary

1. *The characteristic peaks of platinum couldn't be clearly observed in XRD patterns, but the existence of platinum on the Ti_4O_7 support materials was observed in the cyclic voltammogram.*
2. *The different ECSA results of the entire 20% Pt/Ti_4O_7 catalysts was highly influenced by the catalyst ink preparation technique.*
3. *While the ORR activity of the entire 20% Pt/Ti_4O_7 catalysts was lower than the commercial 20% Pt/C catalyst in terms of the onset potential, kinetic current density at 0.9 V vs. RHE and mass activity.*

Conclusion

Conclusion

1. *High surface area Ti_4O_7 was successfully synthesized by utilizing titanium(IV) ethoxide as titanium precursor and PEG 400 as reducing agent.*
2. *The platinum nanoparticles were successfully deposited on Ti_4O_7 support material by utilizing microwave-assisted polyol synthesis.*
3. *The different ECSA results of the entire catalysts were highly influenced by the catalyst ink preparation technique, while the ORR activity of the entire 20% Pt/Ti_4O_7 catalysts was lower than the commercial 20% Pt/C.*
4. *The carbon residue have not been completely removed from the Ti_4O_7 support material.*

Outlook

Outlook

1. *The carbon residue should be removed completely before platinum nanoparticles deposition in order to check its influence in catalytic activity of 20% Pt/Ti_4O_7 catalyst.*
2. *Moreover, another effective and efficient way in removing carbon residue from Ti_4O_7 support material should be developed.*

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1. *Prof. Bing-Joe Hwang who has given me facility and support during the study here.*
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3. *Institut Teknologi Sepuluh Nopember and NTUST who have given me a chance to join the double degree program.*

Mount Bromo

The active volcano in East Java, Indonesia